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Recovery of Strategic Metals from Waste Printed Circuit Boards with Deep Eutectic Solvents and Ionic Liquids

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Abstract: The recycling of metals from waste printed circuit boards (WPCBs) has been presented as a solid–liquid extraction process using two deep eutectic solvents (DESs) and four ionic liquids (ILs). The extraction and separation of Cu(II), Ag(I), and other metals, such as Al(III), Fe(II), and Zn(II), from the solid WPCBs (after the physical, mechanical, and thermal pre-treatments) with different solvents are demonstrated. Two popular DESs were used to recover valuable metal ions: (1) choline chloride + malonic acid, 1:1, and (2) choline chloride + ethylene glycol, 1:2. The extraction efficiencies of DES 1 after two extraction and two stripping stages were only 15.7 wt% for Cu(II) and 17.6 wt% for Ag(I). The obtained results were compared with those obtained with four newly synthetized ILs as follows: didecyldimethylammonium propionate ($[N_{10,10,1,1}][C_2H_5COO]$), didecylmethylammonium hydrogen sulphate ($[N_{10,10,1,H}][HSO_4]$), didecyldimethylammonium dihydrogen phosphate ($[N_{10,10,1,1}][H_2PO_4]$), and tetrabutylphosphonium dihydrogen phosphate ($[P_{4,4,4,4}][H_2PO_4]$). Various additives, such as didecyldimethyl ammonium chloride surfactant, DDACl; hydrogen peroxide, H_2O_2; trichloroisocyanuric acid, TCCA; and glycine or pentapotassium bis(peroxymonosulphate) bis(sulphate), PHM, were used with ILs during the extraction process. The solvent concentration, quantity of additivities, extraction temperature, pH, and solid/liquid, as well as organic/water ratios, and the selectivity and distribution ratios were described for all of the systems. The utilization of DESs and the new ILs with different additives presented in this work can serve as potential alternative extractants. This will help to compare these extractants, additives, extraction efficiency, temperature, and time of extraction with those of others with different formulas and procedures. The metal ion content in aqueous and stripped organic solutions was determined by the ICP-MS or ICP-OES methods. The obtained results all show that solvent extraction can successfully replace traditional hydrometallurgical and pyrometallurgical methods in new technologies for the extraction of metal ions from a secondary electronic waste, WPCBs.

Keywords: spent solid WPCBs; metals extraction/recovery; DESs; ionic liquids

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1. Introduction

Recently, the increasing amount of electronic waste (e-waste) has become a global issue, and it is reported to be the fastest-growing waste stream. It is estimated to have an annual growth rate of over 70 million tons per year. Waste printed circuit boards (WPCBs) constitute about 4–7% of the total mass of e-waste [1]. WPCBs contain metals, such as Au, Cu, Ag, Zn, Al, and Pb, as well as polymers, ceramics, and other substances [2]. Therefore, the resource recovery of metals from WPCBs with an efficient and green method is key to contemporary recycling. Presently, only about 8–12 chemical elements from the list of 60 are being studied for strategic recycling [3–8]. Currently, the consumption of metals has increased, and recycling is an important parameter for metal sustainability. The application of 21st-century solvents—ionic liquids (ILs)—in the recycling of metals has been popular for many years [3]. E-waste generated globally is a source of many metals, such as Cu, Zn, Ni, Al, Fe, Pb, and Sn, as well as precious metals (Au, Ag, Pd, and Pt), and rare earth metals (Y, Eu, Ce, Gd, and La) [8–11]. The most popular methods for recycling metals from WPCBs

are the well-known hydrometallurgical and pyrometallurgical processes [12–14]. Many reviews have been published in the literature on the current status of extraction methods and perspectives [13–28]. These have been presented as physical, mechanical, and thermal pre-treatment steps, followed by physical, pyrolysis, supercritical fluid, pyrometallurgical (smelting-refining), and hydrometallurgical processes with chemical leaching. Various approaches and techniques for the selective recovery of metal elements from the leachate, including ionic liquids, DESs, solvent extraction, electrowinning, adsorption, and different precipitation methods, have been discussed in the literature in recent years ([13–28], and literature cited therein).

WPCBs contain precious metals, like Au(III) and Pd(II), which are separated by cementation with Cu powder from the leaching solutions containing many metals with a mixture of HCl and NaClO and by solvent extraction with bis(2,4,4-trimethylpentyl) phosphinic acid, Cyanex 272 [29]. A new review dedicated to porous structure-based materials for application in the recycling of Au from e-waste has also been published [30]. The reusability, high selectivity, stability, and ease of handling have been presented [30].

A sustainable green and closed-loop method has been proposed for bromine recovery from crude bromine salt by-products of WPCB smelting [31]. WPCBs contain Cu, an important metal in the future global copper cycle in different sectors and research in recent years [32,33].

The hydrometallurgical processing of Cu and Au dissolution from the feed of WPCBs and processed fractions using different lixiviants have been studied [34]. The extraction efficiency for Cu of electrodeposition is 75%. Au can be successfully precipitated from leaching solutions using urea, followed by sodium bisulfide. As a result, 4.1 g of Au and 9 kg of Cu can be recovered from 10 kg of WPCBs [34].

The recovery of gold (Au) from WPCBs derived from discarded mobile phones has been proposed with thiosulfate leaching systems that utilize a cobalt (Co(II))–glycine complex as a catalyst with low thiosulfate consumption and a Au leaching efficiency of 97.8% [35]. The other metals could be extracted using HCl and a H_2SO_4–H_2O_2 system. The recovery of Au from the leachate solution was demonstrated with N1923 [35].

Thiosulfate leaching with nickel-ammonia, cobalt-ammonia, and copper-ammonia catalysis thiosulfate processes were proposed for gold extraction from an oxide gold concentrate. The electrochemical leaching mechanism, combined with XPS and SEM-EDS analyses, has been presented [36]. A systematic review of gold extraction and other aqueous leaching or electrochemical methods has also been presented [37–39].

The two pre-treatment routes to extract (Au, Ag, Cu, etc.) from WPCBs by dimethylacetamide (DMA) at the optimized conditions of T = 423 K for 16 h with a solid–liquid ratio of 3:10 and ultrasonic treatment have been recently presented [40].

The leaching of Cu, Co, Au, and Ag from the WPCBs of cellular phones has been carried out using the imidazolium-based ionic liquids (ILs) 1-butyl-3-methylimidazolium hydrogen sulphate ([BMIM][HSO_4]) and 1-hexyl-3-methylimidazolium hydrogen sulphate ([HMIM][HSO_4]) for Cu and Co extraction, as well as 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]) and 1-butyl-3-methylimidazolium bromide ([BMIM][Br]) for Au and Ag extraction within a temperature range of T = 333–353 K [41]. The extraction efficiency for each metal was as follows: 86.2% for copper, 99.5% for cobalt, 40.8% for gold, and 44.6% for silver [41].

A new solvent extraction procedure has been proposed by many authors using thermal pre-treatment, different leaching procedures, and different ILs with different additives to recover Cu, Ag, Pd, Ni, Al, Au, Fe, and Zn from the solid material of WPCBs [3,5,42–46]. In hydrometallurgical processes for recycling metals, different acids and alkalis are commonly used to extract metals such as copper, gold, silver, and palladium [5]. Copper extraction from solid e-waste without leaching using ammonium and imidazolium-based ILs, e.g., dimethyloctylammonium hydrogen sulphate, [$N_{1,1,8,H}$][HSO_4]/20 wt% H_2O_2 at a temperature of T = 348 K after one hour with a selectivity of 20–33 wt%, has been presented [43]. Copper extraction from solid material at a level of 98% was obtained using hydrogen sulphate ILs as follows:

1-propylsulfonic-3-methylimidazolium hydrogen sulphate ([BMIM][HSO_4]), 1-carboxymethyl-3-mehylimidazolium hydrogen sulphate ([PS-MIM][HSO_4]), diacethylimidazolium hydrogen sulphate ([CM-MIM][HSO_4]), [di-Ac-IM][HSO_4] with the addition of H_2O_2, after the primary extraction with 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]) [44]. The extraction of Cu, Ag, and Au from WPCBs was presented with 1-butyl-3-methylimidazolium bis{(trfluoromethyl)sulfonyl}amide ([BMIM][NTf_2]), 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]), and trihexyltetradecylphosphonium chloride, also known as Cyphos 101 ([$P_{6,6,6,14}$][Cl]), after preliminary leaching with (H_2SO_4 + H_2O_2) and (35% HCl + 55% HNO_3) [45]. The extraction efficiency for copper was at levels of 90% and 99% at the temperature of T = 343 K at pH = 6, with a S/L ratio of 1:1 [45].

In our recent study, extraction with the IL, DESs and Cyanex 272 in the recovery of metals from WPCBs after thermal pre-treatment and leaching with different acids was proposed [46]. For the ILs, the aqueous biphasic system (ABS) method and DESs were used to extract metal ions from the leachate and the solid phase after leaching to the extent of 20–30 wt% of metals [46]. Various methods of recycling valuable metals have been developed with ILs and DESs with different additives, as well as using organophosphorus-based acids, and are presented in many works [14,19,47,48].

In recent studies, the electrodeposition of copper and silver after extraction with ILs has been proposed [49]. One of the popular ILs used for metal extraction from the waste of petroleum catalysts and e-waste is [BMIM][HSO_4] [49]. This IL has been used for the extraction of Cu (82%) and Zn (99%) from brass waste, with the addition of H_2O_2 and $KHSO_5$ at room temperature at an IL/A ratio of 1:1 v/v [49]. The IL [BMIM][HSO_4], with the addition of H_2O_2, was used to extract copper, zinc, and aluminium from spent WPCBs at a temperature of T = 343 K for 2 h [50]. The extraction efficiency of copper was 100% using a solution of 25 cm^3 of 80% IL v/v and 10 cm^3 of 30% H_2O_2 with an S/L ratio of 1:25 g/cm^3 [50]. The ILs with the $[HSO_4]^-$ anion were also used in a recently published work for the extraction of Cu(II) and Ag(I) [51].

ILs and DESs have been used by us for the extraction of metals from aqueous solutions and from the solid phase, such as the "black mass" of Li-ion batteries [52,53]. The DESs {choline chloride + ethylene glycol, 1:2, 1:3, 1:4, and 1:10} with iodine species were currently used as oxidizing agents of e-waste metals [54].

The use of tributylmethylammonium chloride ([$N_{4,4,4,1}$][Cl]) with trichloroizocyanuric acid (TCCA) showed 100% extraction of the metals: Au, Pd, Cu, and Ag at a low temperature of T = 298 K [55]. TCCA is a simple substance used as a cheap oxidant for disinfecting swimming pools. Glycine and sodium cyanide were used for the extraction of metals (Au, Ag, Pd, and Pt) from WPCBs [56], as well as Cu(II) [57]. However, the very inconvenient ratio of S/L= 1:100 was applied with the addition of 10% of H_2O_2 at the temperature T = 303 K for 2 h at pH = 6–6.5 [57]. The extraction efficiency of Cu(II) was 94%. Glycine is known as an amino acid used for the creation of heteronuclear complexes with metal ions.

Pourbaix diagrams for the Cu–S–H_2O, Zn–S–H_2O, or Ni–S–H_2O systems were presented after the leaching of WPCBs with H_2SO_4 and showed the possibility of metal ion extraction [58].

The extraction of approximately 60% aluminium, 94% copper, 76% zinc, 50% nickel, and residual iron from the non-magnetic fraction of WPCBs was obtained using bis-(2-ethylhexyl) hydrogen phosphate, D2EHPA [59]. Initially, 100 wt% Zn, Fe, and Al were retrieved at pH 3.5, 2:1 A/O, 10% (v/v) D2EHPA, and then 100% of the Cu was extracted at pH 3.5, 1:1 A/O, 20% (v/v) D2EHPA in the second stage.

In this work, the extraction of Cu(II), Ag(I), Al(III), Fe(II), and Zn(II) in the solid–liquid extraction of metal ions with various solvents was evaluated. The single- or two-stage extraction of metals from WPCBs after thermal pre-treatment (T = 1023 K) for 7 h was investigated with two DESs as follows: (1) {choline chloride + malonic acid, 1:1} and (2) {choline chloride + ethylene glycol, 1:2}. The extraction ability of four synthetized ILs, such as didecyldimethylammonium propionate ([$N_{10,10,1,1}$][C_2H_5COO]), didecylmethylammonium hydrogen sulphate ([$N_{10,10,1,H}$][HSO_4]), didecyldimethylammonium dihydrogen phosphate

($[N_{10,10,1,1}][H_2PO_4]$), and tetrabutylphosphonium dihydrogen phosphate ($[P_{4,4,4,4}][H_2PO_4]$), is also presented. Different additives such as didecyldimethylammonium chloride surfactant (DDACl), diethyl phosphite ester (DFE), hydrogen peroxide (H_2O_2), trichloroisocyanuric acid (TCCA), glycine or pentapotassium bis(peroxymonosulphate) bis(sulphate), PHM were used.

These processes, consisting mainly of solid–liquid extraction, were carried out at a different pH, temperature, time, and concentration of additives, such as H_2O_2, TCCA, glycine, PHM, and the (S/L) phase ratio. The concentration of metal ions in the aqueous and stripped organic solutions was determined by the ICP-MS or ICP-OES methods.

2. Experimental Design

2.1. Preparation of the Solid Material

The WPCB samples were delivered by Elemental H2Tech Waste Management in Poland. The WPCB blend was used after the process of mechanical destruction. In the next step, the thermal pre-treatment at T = 1023 K for 7 h was carried out in a resistance chamber furnace (IZO), 16.1 kW, as described in our previous work [46] (see Figure 1). The high temperature helps to decompose the bonding force between particles of the material. The collected material was then manually shredded into small particles of a diameter range of 1–2 mm. The determination of the metal content and the apparatus used have been described earlier [46]. The composition of the solid material is presented in Table 1. WPCB samples, which were delivered by Elemental H2Tech Waste Management in Poland, did not contain any gold.

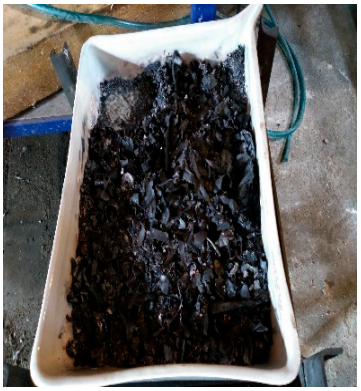


Figure 1. Solid WPCB material after thermal pre-treatment.

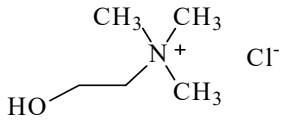
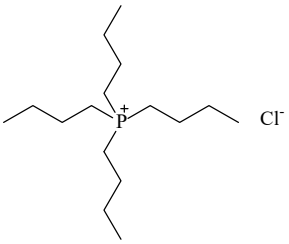
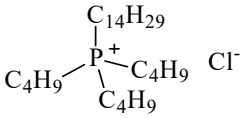
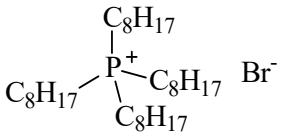
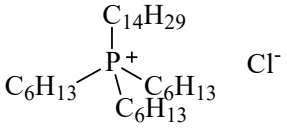
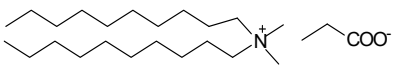
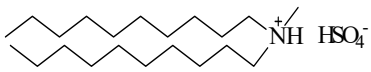
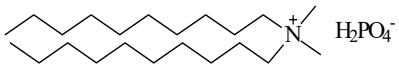
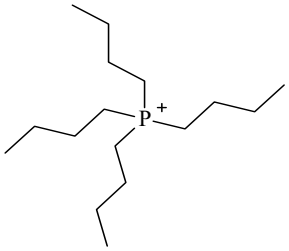
Table 1. Metal content in the starting WPCB material and after thermal pre-treatment at T = 1023 K for 7 h. (microwave digestion/FAAS and ICP-MS methods) [46].

Content of Metals in the Solid Phase					Mass of Sample
Cu(II)	Ag(I)	Al(III)	Fe(II)	Zn(II)	kg
g/kg	mg/kg	g/kg			
Primary material					
224	483	81.9	79.4	18.1	1.000
Primary material after thermal pre-treatment					
335	721	122	119	27.0	0.670

2.2. Chemicals

Basic information on the ILs is listed in Table 2, and on other chemicals, it is listed in Table 3.

Table 2. Data of the ionic liquids used for extraction: structure, name, abbreviation of name, supplier, CAS number, molar mass (M), and mass fraction purity.

Chemical Structure	Name, Abbreviation of Name, Supplier, CAS Number	Molar Mass M/ (g mol^{-1})	Purity * in Mass Percent (%)
	Choline chloride ([$N_{2OH,1,1,1}$][Cl]), Sigma-Aldrich, Darmstadt, Germany, CAS: 67-48-1	139.62	>98
	Tetrabutylphosphonium chloride ([$P_{4,4,4,4}$][Cl]), IoLiTec, Heilbronn, Germany, CAS: 2304-30-5	294.88	>95
	Tributyltetradecylphosphonium chloride ([$P_{4,4,4,14}$][Cl]), IoLiTec, Heilbronn, Germany CAS: 81741-28-8	435.24	>95
	Tetraoctylphosphonium bromide ([$P_{8,8,8,8}$][Br]), IoLiTec, Heilbronn, Germany CAS: 23906-97-0	563.76	>95
	Trihexyltetradecylphosphonium chloride, known as Cyphos IL 101, ([$P_{6,6,6,14}$][Cl]), IoLiTec, Heilbronn, Germany CAS 258864-54-9	519.42	>95
	Didecyldimethylammonium propionate ([$N_{10,10,1,1}$][C_2H_5COO]), synthesized	399.79	>95
	Didecyldimethylammonium hydrogensulphate ([$N_{10,10,1,H}$][HSO_4]), synthesized	409.67	>95
	Didecyldimethylammonium bis(2-ethylhexyl) dihydrogen phosphate ([$N_{10,10,1,1}$][H_2PO_4]), synthesized	423.7	95
	Tetrabutylphosphonium dihydrogen phosphate ([$P_{4,4,4,4}$][H_2PO_4]), synthesized	356.48	95

* As stated by the supplier.

Table 3. Basic data of the chemicals used in the extraction process: name, supplier, CAS number, molar mass (M), and purity.

Name, Molecular Formula, Supplier, CAS Number	Molar Mass ($g \cdot mol^{-1}$)	Purity * in Mass Percent (%)
Malonic acid, $C_3H_4O_4$, Sigma-Aldrich, Darmstadt, Germany, CAS 141-82-2	104.06	99.0
Ethylene glycol, $HOCH_2CH_2OH$, Riedel-de-Haën, Seelze 1, Germany, CAS 107-21-1	62.08	99.0
Didecyldimethylammonium chloride, $[N_{10,10,1,1}][Cl]$, DDACl, Alpinus Sp. z o.o., Solec Kujawski, Poland, CAS 7173-51-5	362.16	50 wt% aq. solution
Trichloroisocyanuric acid (TCCA), Thermo Fisher Scientific, Karlsruhe, Germany, CAS 87-90-1	232.41	99.0
Glycine, $C_2H_5NO_2$, Sigma-Aldrich, Heilbronn, Germany, CAS 56-40-6	75.07	99.0
Pentapotassium bis(peroxymonosulphate)bis(sulphate) PHM, $(2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4)$, Sigma-Aldrich, Heilbronn, Germany, CAS 70693-62-8	614.76	98.0
Sulphuric acid, H_2SO_4, Riedel-de Haën, Seelze 1, Gemany, CAS 7664-93-9	98.08	96.0
Sodium chloride, NaCl, Chempur, Karlsruhe, Germany, CAS 7647-14-5	58.44	99.9
Sodium sulphate, Na_2SO_4, Chempur, Karlsruhe, Germany, CAS 7757-82-6	142.04	99.0

* As stated by the supplier.

Taking into consideration the economic prospects for the recovery of valuable metals, two DESs were tested as follows: DES 1 (choline chloride, $[N_{2OH,1,1,1}][Cl]$ + malonic acid, 1:1 [60]) and DES 2 (choline chloride, $[N_{2OH,1,1,1}][Cl]$ + ethylene glycol, 1:2 [61]). The $[N_{2OH,1,1,1}][Cl]$ used for the synthesis of DESs was dried under reduced pressure (10 hPa) at T = 323 K for 8 h.

All the ILs used in the extraction were dried for 72 h at T = 340 K under reduced pressure, p = 6 kPa, and analyzed by Karl–Fischer titration (Metrohm, Herisau, Switzerland, 716 DMS Titrino) to obtain information about the exact mass of the added IL. The water content was less than 760×10^{-6} g with an uncertainty of u(w.c.) = 10×10^{-6} g. The uncertainty of the temperature measurements was ±0.1 K. The Mettler Toledo AB 204-S balance, with an accuracy of $\pm 1 \times 10^{-4}$ g, was used. The pH was measured by litmus bromothymol blue papers in a small reactor.

2.3. Recovery Procedure

A mixture of 15 cm^3 of DES 1 or DES 2, 1.5 g of the black powder, 8 cm^3 of DDACl (50 wt% aqueous solution), 4 cm^3 of H_2O_2 (30 wt% aqueous solution), and 3 cm^3 of water was stirred with a coated magnetic stirring bar under reflux for 2 h, 3000 rpm at T = 333 K, and pH = 5. After the sedimentation of the residual solid phase, the solid material was dried at a temperature of T = 323 K for 5 h, and in many experiments, a second extraction stage was proposed using the same proportion of the solid phase, DES, and additives as above. The volumetric ratio of the organic to aqueous phase was O/A = 1:1. The solid WPCB material to liquid (S/L) ratio was 1.5:30 g/cm^3. The solid phase to DDACl surfactant (S/DDACl) ratio was kept at 1.5:8 g/cm^3. The liquid phases (DES 1: 27 cm^3 of the aqueous lower phase and 3 cm^3 of the organic upper phase; DES 2: 44 cm^3 of the aqueous lower phase and 9 cm^3 of the organic upper phase) were mixed together after two extractions and

analyzed for the content of metal ions. It may be observed that during the process, a large amount of the DES is in the aqueous phase.

Extraction with the $[N_{10,10,1,1}][C_2H_5COO]$ or $[N_{10,10,1,H}][HSO_4]$ ILs was performed as follows: 16 g of the IL was added to 1.5 g of the black powder, 8 cm^3 of DDACl (50 wt% aqueous solution), 8 cm^3 of H_2O_2 (30 wt% aqueous solution), and 10 cm^3 of water. The process was carried out for 3 h at 3000 rpm at T = 333 K at pH = 6 or 1.5-3 for $[N_{10,10,1,H}][HSO_4]$. The ratio O/A = 0.6. The (S/L) ratio was kept at 1.5:42 g/cm^3. After the sedimentation process, the solid phase was dried at the temperature T = 323 K for 5 h, and the second extraction stage was carried out as described above. The acidic aqueous phases were mixed together and analyzed as follows: For $[N_{10,10,1,1}][C_2H_5COO]$, one phase of 32 cm^3 in the single-extraction stage and 46 cm^3 in the two-extraction stage; $[N_{10,10,1,H}][HSO_4]$: 36 cm^3 of the lower phase and 47 cm^3 of the upper phase.

The extraction procedure with the $[N_{10,10,1,1}][H_2PO_4]$ and $[P_{4,4,4,4}][H_2PO_4]$ ILs was performed as described above. The solid-to-liquid (S/L) ratio was kept at 1.5:42 g/cm^3. Only a single phase was obtained after extraction. After sedimentation, the solid phase was dried at a temperature of T = 323 K for 5 h. The single- and two-extraction stages were used for these two ILs. After the two-extraction stage, the acidic aqueous phases were combined and analyzed (single phase: 36 cm^3 in the single-extraction stage and 58 cm^3 in the two-extraction stage).

Extraction with the addition of the oxidizing agent TCCA was performed using the following ILs: $[P_{4,4,4,4}][Cl]$, $[P_{4,4,4,14}][Cl]$, $[P_{8,8,8,8}][[Br]$, $[P_{6,6,6,14}][Cl]$, $[N_{10,10,1,1}][C_2H_5COO]$, $[N_{10,10,1,H}][HSO_4]$, $[N_{10,10,1,1}][H_2PO_4]$, or $[P_{4,4,4,4}][H_2PO_4]$. A total amount of 16 g of the IL was added to 1.5 g of the black powder, 10 cm^3 of water, 8 cm^3 of DDACl (50 wt% aqueous solution), and 4 g, 8 g or 12 g of TCCA and 11, 22, or 33 cm^3 of acetone, respectively. The O/A ratio = 2:1. The (S/L) ratio was kept at 1.5:55 g/cm^3. The extraction process was run for 2 h at 3000 rpm at T = 318 K, pH = 2. A single aqueous phase, or a single organic phase ($[P_{6,6,6,14}][Cl]$), or two phases ($[P_{8,8,8,8}][[Br]$ O/A phases, 29 cm^3/22 cm^3; $[N_{10,10,1,H}][HSO_4]$ O:A phases, 27 cm^3/78 cm^3) were obtained after the extraction. The acidic aqueous phase and the stripped (with sulphuric acid, 1.2 M H_2SO_4 at T = 323 K for 20 min.) organic phase were analyzed. The second extraction of metal ions from the solid material that was dried at a temperature of T = 323 K for 5 h was carried out with $[P_{4,4,4,4}][Cl]$, $[P_{4,4,4,14}][Cl]$, $[P_{8,8,8,8}][[Br]$, $[P_{6,6,6,14}][Cl]$, and $[N_{10,10,1,1}][H_2PO_4]$.

The addition of glycine and H_2O_2 was performed using the following ILs: $[P_{4,4,4,4}][Cl]$, $[P_{8,8,8,8}][Br]$, or $[N_{10,10,1,1}][C_2H_5COO]$. A total amount of 16 g of the IL was added to 1.5 g of the black powder, 8 cm^3 of DDACl (50 wt% aqueous solution), 4 cm^3 of H_2O_2 (30 wt% aqueous solution), 10 cm^3 of water, and 4 g or 12 g of glycine. The extraction process, as in the previous case, was carried out for 2 h at 3000 rpm at T = 333 K, pH = 6. The O/A ratio = 0.9–1.3. The (S/L) ratio was kept at 1.5:42–50 g/cm^3. A single phase was obtained after the extraction. The acidic aqueous phase was analyzed (one phase of 31–40 cm^3 in single-extraction stage).

Extraction with the addition of PHM was performed using the only two ILs found to be the best in previous IL treatments, such as $[P_{4,4,4,4}][Cl]$ or $[P_{4,4,4,14}][Cl]$. A total amount of 16 g of the IL was added to 1.5 g of the black powder, 8 cm^3 of DDACl (50 wt% aqueous solution), and 4 g, 8 g, or 16 g of PHM and 14 cm^3 of water at a time of 2 h, 3000 rpm at T = 333 K, pH = 3. The O/A ratio = 0.6–0.4. The (S/L) ratio was kept at 1.5:42–54 g/cm^3. Two extraction stages were carried out. The two phases obtained after extraction were analyzed as follows: ($[P_{4,4,4,4}][Cl]$, 76/6 cm^3, 98/16 cm^3, 83/49 cm^3 organic phase/aqueous phase for 4 g, 8 g, and 16 g of PHM, respectively, and $[P_{4,4,4,14}][Cl]$, 49/30 cm^3 organic phase/aqueous phase for 4 g of PHM). The O/A ratio = 1:1.

2.4. Synthesis of ILs

The synthesis of $[N_{10,10,1,1}][C_2H_5COO]$, $[N_{10,10,1,H}][HSO_4]$, $[N_{10,10,1,1}][H_2PO_4]$, and $[P_{4,4,4,4}][H_2PO_4]$ are presented together with the NMR spectra (recorded on the spectrom-

eter at 300 MHz in the presence of tetramethyl silane (TMS) as an internal standard in Figures S1–S4 in the Supplementary Materials) [62].

3. Results and Discussion

3.1. Solid WPCBs' Content

The metal content in spent WPCB material after thermal pre-treatment, obtained with microwave digestion/FAAS and the ICP-MS method, is listed in Table 1 [46].

The starting WPCB solid material contained the following metals: aluminium (Al), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), silver (Ag), and lead (Pb). The metal content was in the range of 1–220 g/kg and only the content of silver was much lower, 483 mg/kg. The solid material reduced in weight after the thermal pre-treatment process, and the Cu and Ag contents were 335g/kg and 721 mg/kg, respectively [46].

3.2. Extraction with DESs and ILs

The metal extraction efficiency (E) from the solid to liquid phases (the leaching process) and the distribution ratio (D) were calculated according to the following equations:

$$E\ (\text{wt\%}) = 100 \times (g_{E,A} + g_{E,O})/g_0 \quad (1)$$

$$D = (g_{E,A} + g_{E,O})/g_0 \quad (2)$$

where g_0 (g) is the metal content in the black powder, $g_{E,A}$ (g) is the amount of metal ions in the aqueous phase (A), and $g_{E,O}$ (g) is the organic phase (O) after extraction.

The DES 1 or DES 2 solution was used directly in the extraction from the solid phase. The two-extraction stage with DES 1 led to an effective but simultaneous extraction of all metal ions, including Cu(II) and Ag(I) ions, at a low temperature of T = 333 K and for a short period of time, 2 h at pH = 5, E_{Cu} = 15.7 wt%, D_{Cu} = 0.2, and E_{Ag} = 17.6 wt%, D_{Ag}= 0.2. The results, presented in Table 4, also indicate a higher extraction of other metals such as aluminium, E_{Al} = 47.5 wt%, D_{Al} = 0.5, and iron E_{Fe} = 47.9 wt%, D_{Fe} = 0.5.

Table 4. Results of metals extraction with DESs at T = 333 K, extraction efficiency, E (wt%), distribution ratio, D, and pH of the aqueous phase after the two-extraction stage.

Extracting Solvent	Ion	g_0 * (mg)	g_E * (mg)	E (wt%)	D	pH
DES 1 + H_2O_2	Cu(II)	502.50	78.73	15.7	0.2	5
	Ag(I)	1.082	0.191	17.6	0.2	
	Al(III)	183.00	86.89	47.5	0.5	
	Fe(II)	178.50	85.46	47.9	0.5	
	Zn(II)	40.50	5.45	13.5	0.1	
DES 2 + H_2O_2	Cu(II)	502.50	21.13	4.2	0	5
	Ag(I)	1.082	0.09	8.3	0	
	Al(III)	183.00	60.98	33.3	0.3	
	Fe(II)	178.50	15.76	8.8	0	
	Zn(II)	40.50	3.03	7.5	0	

g_0 *—metal content in the solid phase before the extraction; g_E *—metal ion content in the aqueous phase after extraction and from the organic phase after stripping.

A high solubility of the solid material in DES 1 during the extraction processes was observed. These results confirm that DES 1 is suitable for the extraction of metals from the solid phase to the liquid phase with a high extraction efficiency in the presence of H_2O_2 and the surfactant DDACl. However, the separation of particular metal anions was unsuccessful. Unfortunately, the extraction efficiency using DES 2 was not attractive, and

only the extraction of aluminium was on a level of E_{Al} = 33.3 wt%, D_{Al} = 0.3. This means that DES 2 may only be used for the extraction of Al(III) at low temperatures and for a short duration.

The hypothesized mechanisms of recovery of metal ions from the aqueous (A) to the organic (O) DES 1 phase are proposed as an "ion exchange" or/and of an "ion pairing" extraction process as follows:

$$2\ Me^{+}_{(A)} + [Cl]^{-}_{(A)} + [COO]^{-}_{(O)} = MeCl_{(A)} + Me[COO]_{(O)} \quad (3)$$

This mechanism has been proposed in the literature for the extraction of metal ions from the solid material to the liquid leachate acidic phase in the presence of H_2O_2 [63].

The synthetized IL $[N_{10,10,1,1}][C_2H_5COO]$ was very attractive for the extraction of silver, as follows: E_{Ag} = 101 wt%, D_{Ag} = 1 after the single-extraction stage, and E_{Ag} = 108 wt%, D_{Ag} = 1 after the two-extraction stage at the low temperature of T = 333 K. This IL also exhibited over 50 wt% extraction efficiency for Zn (67.2–71.9 wt%) after a single- or two-extraction stage. The results are listed in Table 5.

Table 5. Results of single- or two-extraction stage metal extraction with $[N_{10,10,1,1}][C_2H_5COO]$ and $[N_{10,10,1,H}][HSO_4]$ at T = 333 K, extraction efficiency, E (wt%), distribution ratio, D, and pH of the aqueous phase after extraction.

Extracting Solvent	Ion	g_0 * (mg)	g_E * (mg)	E (wt%)	D	pH
$[N_{10,10,1,1}][C_2H_5COO] + H_2O_2$ (single-extraction stage)	Cu(II)	502.50	48.45	9.6	0	6
	Ag(I)	1.082	1.096	100	1	
	Al(III)	183.00	37.12	20.3	0.2	
	Fe(II)	178.50	23.84	13.3	0.1	
	Zn(II)	40.50	27.23	67.2	0.7	
$[N_{10,10,1,1}][C_2H_5COO] + H_2O_2$ (two-extraction stage)	Cu(II)	502.50	69.45	13.8	0.1	6
	Ag(I)	1.082	1.168	100	1	
	Al(III)	183.00	54.34	29.7	0.3	
	Fe(II)	178.50	24.32	13.6	0.1	
	Zn(II)	40.50	29.11	71.9	0.7	
$[N_{10,10,1,H}][HSO_4] + H_2O_2$ (two-extraction stage)	Cu(II)	502.50	113.35	22.6	0.2	3–1.5
	Ag(I)	1.082	0.555	51.3	0.5	
	Al(III)	183.00	108.24	59.1	0.6	
	Fe(II)	178.50	21.57	12.8	0.1	
	Zn(II)	40.50	5.93	14.6	0.1	

g_0 *—metal content in the solid phase before the extraction; g_E *—metal ion content in the aqueous phase after extraction.

The synthetized ($[N_{10,10,1,H}][HSO_4] + H_2O_2$) exhibited an extraction of only a little above 50 wt% for silver, E_{Ag} = 51.3 wt%, D_{Ag} = 0.5, and aluminium, E_{Al} = 59.1 wt%, D_{Al} = 0.6, after the two-extraction stage (see Table 5). It is well-known from the literature that imidazolium-based ILs [BMIM][HSO_4], [HMIM][HSO_4], [BMIM][Cl], and [BMIM][Br] have shown an extraction efficiency for copper at 86.2 wt% and for silver at only 44.6 wt% [41]. Using [BMIM][HSO_4] + H_2O_2, the extraction of Cu was 82 wt%, Zn (99 wt%) [49], and Cu (100 wt%) [50]. It can be easily observed that changing the cation of the IL leads to a higher extraction efficiency for copper and silver.

The synthetized ILs with the $[H_2PO_4]^-$ anion revealed an extraction of silver at a level of E_{Ag} = 20.7 wt%, D_{Ag} = 0.2 with ($[N_{10,10,1,1}][H_2PO_4] + H_2O_2$) after the two-extraction stage at a low temperature of T = 333 K. The second IL with this anion, $[P_{4,4,4,4}][H_2PO_4]$, exhibited

a low extraction efficiency for Cu, Al, and Zn after the two-extraction stage. An average value of the extraction efficiency was observed for copper, E_{Cu} = 11.4 wt%, D_{Cu} = 0.1 (see Table 6). Thus, the long aliphatic chains at the cation of the IL ($[N_{10,10,1,1}][H_2PO_4]$), proposed as the additional influence of the surfactant on the extraction from the solid phase, were not very attractive with this anion [63]. The extraction efficiency after the single- or two-extraction stages for DES 1, DES 2, and different ILs + H_2O_2 at T = 318–333 K for 2–3 h, 3000 rpm, and at different pHs is summarized in Figure 2.

Table 6. Results of single- or two-extraction stage of metal extraction with ILs with $[H_2PO_4]^-$ anion at T = 333 K, extraction efficiency, E (wt%), distribution ratio, D, and pH of the aqueous phase after extraction.

Extracting Solvent	Ion	g_0 * (mg)	g_E * (mg)	E (wt%)	D	pH
$[N_{10,10,1,1}][H_2PO_4] + H_2O_2$ (single-extraction stage)	Cu(II)	502.50	15.33	3.0	0	5.5
	Ag(I)	1.082	0.214	19.8	0.2	
	Al(III)	183.00	0.58	0.32	0	
	Fe(II)	178.50	0.116	0.06	0	
	Zn(II)	40.50	2.04	5.0	0	
$[N_{10,10,1,1}][H_2PO_4] + H_2O_2$ (two-extraction stage)	Cu(II)	502.50	22.56	4.5	0	5.5
	Ag(I)	1.082	0.224	20.7	0.2	
	Al(III)	183.00	0.433	0.24	0	
	Fe(II)	178.50	0.163	0.09	0	
	Zn(II)	40.50	4.25	10.5	0.1	
$[P_{4,4,4,4}][H_2PO_4] + H_2O_2$ (single-extraction stage)	Cu(II)	502.50	30.15	6.0	0	6
	Ag(I)	1.082	0.089	8.2	0	
	Al(III)	183.00	17.78	9.7	0	
	Fe(II)	178.50	5.22	2.9	0	
	Zn(II)	40.50	3.94	9.7	0	
$[P_{4,4,4,4}][H_2PO_4] + H_2O_2$ (two-extraction stage)	Cu(II)	502.50	57.17	11.4	0.1	6
	Ag(I)	1.082	0.104	9.6	0	
	Al(III)	183.00	25.31	13.8	0.1	
	Fe(II)	178.50	5.72	3.2		
	Zn(II)	40.50	4.68	11.6	0.1	

g_0 *—metal content in the solid phase before the extraction; g_E *—metal ion content in the aqueous phase after extraction.

The extraction process of silver, for example, from the solid WPCB material in the presence of the proposed ILs and H_2O_2 may be interpreted as similar to the extraction of Cu from the solid material as follows:

$$2\ Ag + 2\ [N_{10,10,1,1}][C_2H_5COO] + H_2O_2 + 2\ H^+ = 2\ Ag[C_2H_5COO] + 2\ H_2O + 2\ [N_{10,10,1,1}]^+ \quad (4)$$

According to reaction (4), the ions of metals (for example, Ag^+) enter into the solution.

The obtained results of the extraction with various ILs with the addition of the oxidizing agent TCCA at a low temperature of T = 333 K were very successful. The choice of a suitable solvent and a special additive is always crucial [64]. The results of the extraction of Ag(I) with ($[P_{4,4,4,4}][Cl]$ + TCCA, 4 g, single-extraction stage) and with ($[P_{4,4,4,4}][Cl]$ + TCCA, 8g, two-extraction stage) are the same, E_{Ag} = 100 wt%, D_{Ag} = 1. A lower extraction efficiency of Cu(II) from the solid material was also observed with ($[P_{4,4,4,4}][Cl]$ + TCCA, 4 g, single-extraction stage), having an efficiency of E_{Cu} = 53.2 wt%,

D_{Cu} = 0.5, and with ([$P_{4,4,4,4}$][Cl] + TCCA, 8g, two-extraction stage), E_{Cu} = 68.9 wt%, D_{Cu} = 0.7. The IL [$P_{4,4,4,4}$][Cl] is much more effective than [$P_{8,8,8,8}$][Br] and [$P_{6,6,6,14}$][Cl] under the same conditions. The best result of aluminium extraction was obtained with ([$P_{4,4,4,4}$][Cl] + TCCA, 8 g, two-extraction stage): E_{Al} = 81,3 wt%, D_{Al} = 0.8, and with ([$P_{4,4,4,14}$][Cl] + TCCA, 8 g, two-extraction stage): E_{Al} = 82,3 wt%, D_{Al} = 0.8. The extraction efficiency of Ag(I) under the same conditions was E_{Ag} = 100 wt%, D_{Ag} = 1. While reviewing Table 7, we can observe that the extraction efficiency of silver is E_{Ag} = 100 wt%, D_{Ag} = 1 using ([$N_{10,10,1,1}$][H_2PO_4] + TCCA, 4 g, single-extraction stage), and of the remaining metal ions, with ([$N_{10,10,1,1}$][C_2H_5COO] + TCCA, 8g, two-extraction stage), was E_{Cu} = 50.1 wt%, D_{Ag} = 0.5; E_{Ag} = 100 wt%, D_{Ag} = 1; and of aluminum, it was E_{Al} = 52.5 wt%, D_{Al} = 0.5. Increasing the amount of TCCA to 12 g in the single-extraction stage did not lead to better results in the extraction efficiency of metal ions. The use of ([$N_{10,10,1,H}$][HSO_4] + TCCA, 8 g, two-extraction stage) revealed a high extraction efficiency only for aluminum, E_{Al} = 83 wt%, D_{Al} = 0.8. The complete results are listed in Table 7. In comparison, the use of [$N_{4,4,4,1}$][Cl] with the addition of TCCA showed a 100% extraction of the metals Au, Pd, Cu, and Ag at a low temperature of T = 298 K [55].

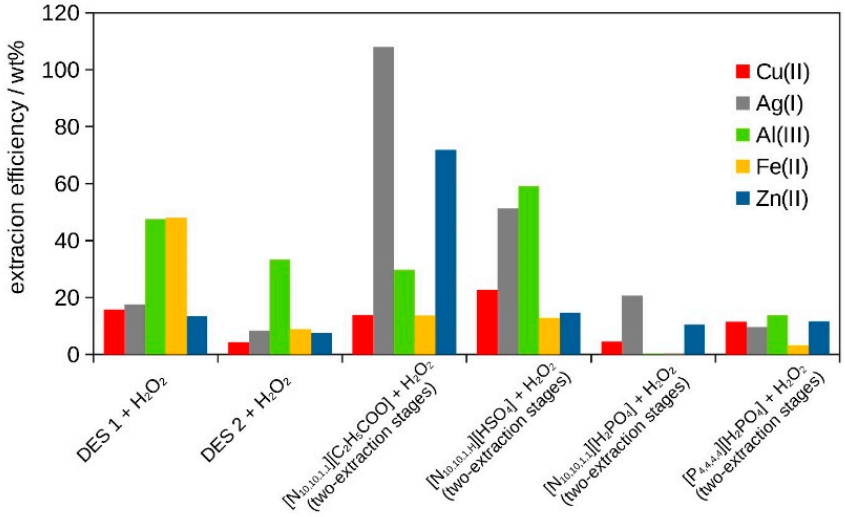


Figure 2. Extraction efficiency (wt%) after single- or two-extraction stages with DES 1, DES 2, and different ILs + H_2O_2. The extraction at each cycle was performed at T = 318-333 K for 2–3 h at 3000 rpm at different pHs.

Table 7. Results of single- or two-extraction stage of metals with ILs and TCCA at T = 333 K, extraction efficiency, E (wt%), distribution ratio, D, and pH of the aqueous phase after extraction.

Extracting Solvent	Ion	g_0 * (mg)	g_E * (mg)	E (wt%)	D	pH
[$P_{4,4,4,4}$][Cl] + TCCA (4 g) (single-extraction stage)	Cu(II)	502.50	267.6	53.2	0.5	2
	Ag(I)	1.082	1.10	100	1	
	Al(III)	183.00	92.0	50.3	0.5	
	Fe(II)	178.50	62.4	35.0	0.3	
	Zn(II)	40.50	10.5	25.9	0.3	
[$P_{4,4,4,4}$][Cl] + TCCA (8 g) (two-extraction stage)	Cu(II)	502.50	346.4	68.9	0.7	2
	Ag(I)	1.082	1.08	100	1	
	Al(III)	183.00	148.7	81.3	0.8	
	Fe(II)	178.50	45.4	25.4	0.2	
	Zn(II)	40.50	17.7	43.7	0.4	

Table 7. *Cont.*

Extracting Solvent	Ion	g_0 * (mg)	g_E * (mg)	E (wt%)	D	pH
$[P_{4,4,4,4}][Cl]$ + TCCA (12 g) (single-extraction stage)	Cu(II)	502.50	190.1	37.8	0.4	2
	Ag(I)	1.082	1.122	100	1	
	Al(III)	183.00	80.79	44.1	0.4	
	Fe(II)	178.50	29.24	16.4	0.2	
	Zn(II)	40.50	4.69	11.6	0.1	
$[P_{4,4,4,14}][Cl]$ + TCCA (8 g) (two-extraction stage)	Cu(II)	502.50	197.1	39.2	0.4	2
	Ag(I)	1.082	1.09	100	1	
	Al(III)	183.00	150.6	82.3	0.8	
	Fe(II)	178.50	29.57	16.6	0.2	
	Zn(II)	40.50	8.74	21.6	0.2	
$[P_{8,8,8,8}][Br]$ + TCCA (8 g) (single-extraction stage)	Cu(II)	502.50	124.08	24.7	0.2	3
	Ag(I)	1.082	0.284	26.2	0.3	
	Al(III)	183.00	54.85	30.0	0.3	
	Fe(II)	178.50	12.40	6.9	0	
	Zn(II)	40.50	1.79	4.4	0	
$[P_{8,8,8,8}][Br]$ + TCCA (8 g) (two-extraction stage)	Cu(II)	502.50	154.5	30.7	0.3	3
	Ag(I)	1.082	0.36	33.3	0.3	
	Al(III)	183.00	62.81	34.3	0.3	
	Fe(II)	178.50	13.73	7.7	0	
	Zn(II)	40.50	2.16	5.3	0	
$[P_{6,6,6,14}][Cl]$ + TCCA (4 g) (organic phase after the demineralization)(single-extraction stage)	Cu(II)	502.50	100.7	20.0	0.2	2
	Ag(I)	1.082	0.30	27.7	0.3	
	Al(III)	183.00	66.18	36.2	0.4	
	Fe(II)	178.50	72.12	40.4	0.4	
	Zn(II)	40.50	7.54	18.6	0.2	
$[N_{10,10,1,1}][C_2H_5COO]$ + TCCA (4 g) (two-extraction stage)	Cu(II)	502.50	147.6	29.4	0.3	2
	Ag(I)	1.082	0.12	11.1	0.1	
	Al(III)	183.00	38.11	20.8	0.2	
	Fe(II)	178.50	8.96	5.0	0	
	Zn(II)	40.50	3.76	9.3	0	
$[N_{10,10,1,1}][C_2H_5COO]$ + TCCA (8 g), (two-extraction stage)	Cu(II)	502.50	251.6	50.1	0.5	2
	Ag(I)	1.082	1.08	100	1	
	Al(III)	183.00	96.05	52.5	0.5	
	Fe(II)	178.50	19.6	11.0	0.1	
	Zn(II)	40.50	13.0	32.1	0.3	
$[N_{10,10,1,1}][C_2H_5COO]$ + TCCA (12 g), (single-extraction stage)	Cu(II)	502.50	133.4	26.5	0.3	2
	Ag(I)	1.082	0.347	32.1	0.3	
	Al(III)	183.00	80.58	44.0	0.4	
	Fe(II)	178.50	15.72	8.8	0	
	Zn(II)	40.50	8.40	20.7	0.2	

Table 7. *Cont.*

Extracting Solvent	Ion	g_0 * (mg)	g_E * (mg)	E (wt%)	D	pH
$[N_{10,10,1,1}][H_2PO_4]$ + TCCA(4 g) (single-extraction stage)	Cu(II)	502.50	199.8	39.8	0.4	2
	Ag(I)	1.082	1.14	100	1	
	Al(III)	183.00	98.8	54.0	0.5	
	Fe(II)	178.50	23.1	12.9	0.1	
	Zn(II)	40.50	8.3	20.5	0.2	
$[N_{10,10,1,H}][HSO_4]$ + TCCA (8 g) (two-extraction stage)	Cu(II)	502.50	118.8	23.6	0.2	1.5
	Ag(I)	1.082	0.417	38.6	0.4	
	Al(III)	183.00	151.8	83.0	0.8	
	Fe(II)	178.50	72.75	40.8	0.4	
	Zn(II)	40.50	8.28	20.5	0.2	

g_0 *—metal content in the solid phase before the extraction; g_E *—metal ion content in the aqueous phase after extraction.

The extraction efficiency after single- or two-extraction stages for different ILs + TCCA (4 g or 8 g) at T = 318 K for 2 h at 3000 rpm, pH = 1.5–3, is presented in Figure 3.

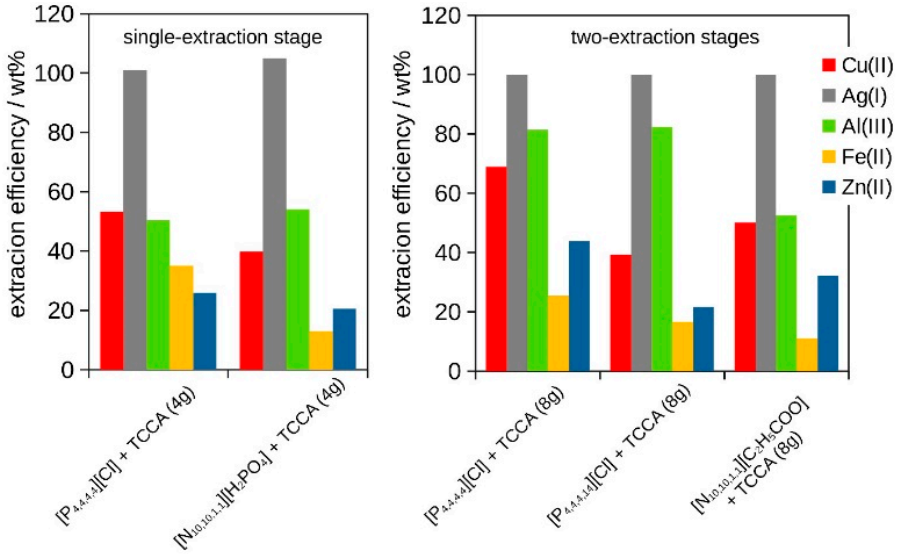


Figure 3. Extraction efficiency (wt%) after single- or two-extraction stages with different ILs + TCCA (4 g or 8 g). The extraction at each cycle was performed at T = 318 K for 2 h at 3000 rpm, pH = 1.5–3.

The single-extraction stage with the addition of glycine and H_2O_2 exhibited a hundred percent efficiency of the extraction of silver using ($[P_{8,8,8,8}][Br]$ + glycine, 4 g) and ($[P_{4,4,4,4}][Cl]$, or $[N_{10,10,1,1}][C_2H_5COO]$ + glycine, 12 g); see Table 8.

Glycine and NaCN were used for the extraction of metals (Au, Ag, Pd, and Pt) [56] and of Cu(II) [57] from the WPCBs (S/L= 1:100) using 10% of H_2O_2 at the temperature T = 303 K for 2 h, pH = 6–6.5, and exhibited an extraction efficiency of Cu(II) 94 wt% [57]. This is a much better result for the extraction of copper than in our experiments, but the use of NaCN and such a large volume of liquid phase is neither economical nor green.

The extraction of Ag(I) with ($[P_{4,4,4,4}][Cl]$ + PHM, 16 g, two-extraction stages) was E_{Ag} = 71.2 wt%, D_{Ag} = 0.7, while at the same time, the low efficiency of Cu(II) extraction was observed, E_{Cu} = 21.2 wt%, D_{Cu} = 0.2 (see Table 9).

Table 8. Results of single-extraction stages of metals with ILs and (glycine + H_2O_2) at T = 333 K, extraction efficiency, E (wt%), distribution ratio, D, and pH of the aqueous phase after the single extraction stage.

Extracting Solvent	Ion	g_0 * (mg)	g_E * (mg)	E (wt%)	D	pH
$[P_{4,4,4,4}][Cl]$ + glycine (4 g)	Cu(II)	502.50	25.88	5.1	0	6
	Ag(I)	1.082	0.086	8.0	0	
	Al(III)	183.00	1.48	0.8	0	
	Fe(II)	178.50	1.87	1.0	0	
	Zn(II)	40.50	1.40	3.4	0	
$[P_{4,4,4,4}][Cl]$ + glycine (12 g)	Cu(II)	502.50	48.40	9.6	0	6
	Ag(I)	1.082	1.09	100	1	
	Al(III)	183.00	12.80	7.0	0	
	Fe(II)	178.50	9.84	5.5	0	
	Zn(II)	40.50	14.69	36.3	0.4	
$[P_{8,8,8,8}][Br]$ + glycine (4 g)	Cu(II)	502.50	35.28	7.02	0	6
	Ag(I)	1.082	1.072	100	1	
	Al(III)	183.00	17.22	9.41	0	
	Fe(II)	178.50	8.79	4.92	0	
	Zn(II)	40.50	2.832	6.99	0	
$[N_{10,10,1,1}][C_2H_5COO]$ + glycine (12 g)	Cu(II)	502.50	25.52	5.1	0	6
	Ag(I)	1.082	1.16	100	1	
	Al(III)	183.00	54.80	29.9	0.3	
	Fe(II)	178.50	7.32	4.1	0	
	Zn(II)	40.50	13.24	32.7	0.3	

g_0 *—metal content in the solid phase before the extraction; g_E *—metal ion content in the aqueous phase after extraction.

Table 9. Results of two-stage extraction of metals with ILs and PHM at T = 333 K, extraction efficiency, E (wt%), distribution ratio, D, and pH of the aqueous phase after the two-extraction stage.

Extracting Solvent	Ion	g_0 * (mg)	g_E * (mg)	E (wt%)	D	pH
$[P_{4,4,4,4}][Cl]$ + PHM (4g) (2 phases)	Cu(II)	502.50	62.3	12.4	0.1	3
	Ag(I)	1.082	0.07	6.5	0	
	Al(III)	183.00	8.52	4.6	0	
	Fe(II)	178.50	18.28	10.2	0.1	
	Zn(II)	40.50	3.58	8.8	0	
$[P_{4,4,4,4}][Cl]$ + PHM (8g) (2 phases)	Cu(II)	502.50	120.5	24.0	0.2	3
	Ag(I)	1.082	0.136	12.6	0.1	
	Al(III)	183.00	12.47	6.8	0	
	Fe(II)	178.50	16.81	9.4	0	
	Zn(II)	40.50	5.73	14.1	0.1	

Table 9. *Cont.*

Extracting Solvent	Ion	g_0 * (mg)	g_E * (mg)	E (wt%)	D	pH
$[P_{4,4,4,4}][Cl]$ + PHM (16g) (2 phases)	Cu(II)	502.50	106.5	21.2	0.2	3
	Ag(I)	1.082	0.770	71.2	0.7	
	Al(III)	183.00	41.29	22.6	0.2	
	Fe(II)	178.50	23.29	13.0	0.1	
	Zn(II)	40.50	3.56	8.8	0	
$[P_{4,4,4,14}][Cl]$ + PHM (4g) (2 phases)	Cu(II)	502.50	19.81	3.9	0	3
	Ag(I)	1.082	0.206	19.1	0.2	
	Al(III)	183.00	28.18	15.4	0.1	
	Fe(II)	178.50	47.64	26.7	0.3	
	Zn(II)	40.50	19.19	47.4	0.5	

g_0 *—metal content in the solid phase before the extraction; g_E *—metal ion content in the aqueous phase after extraction.

The content of additives was at a level of 2–12 g or only 16 g for PHM/1.5 g of WPCB solid material. In order to increase the extraction efficiency, a much larger amount of additives is probably needed, which will generate higher costs.

The results of the extraction of metals with {Cyanex 272) + diethyl phosphite ester + H_2O_2} and with {D2EHPA + diethyl phosphite ester + H_2O_2} after the two-extraction stage at T = 333 K, pH = 5–6, have shown an extraction efficiency for comparison, E_{Cu} = 16.0 wt% and E_{Cu} = 20.1 wt%, respectively (not shown in this work).

4. Conclusions

Various methods for the extraction of metal ions from waste printed circuit board (WPCBs) powder after the process of cutting them into small pieces, crushing in a hydraulic press, and finally, thermal pre-treatment at a temperature of T = 1023 K for 7 h, have been presented. The synthesis of two DESs (1) {choline chloride + malonic acid, 1:1} and (2) {choline chloride + ethylene glycol, 1:2} and four new ILs, such as didecyldimethylammonium propionate ($[N_{10,10,1,1}][C_2H_5COO]$), didecylmethylammonium hydrogen sulphate ($[N_{10,10,1,H}][HSO_4]$), didecyldimethylammonium dihydrogen phosphate, ($[N_{10,10,1,1}][H_2PO_4]$), and tetrabutylphosphonium dihydrogen phosphate ($[P_{4,4,4,4}][H_2PO_4]$), are also presented. The efficiency of the extraction of various metals such as Cu(II), Ag(I), Al(III), Fe(II), and Zn(II) from solid material to the liquid phase with DES 1, DES 2, and ILs, with the addition of H_2O_2, TCCA, PHM, or glycine after a single- or two-extraction stage, is presented. Finally, a 100% extraction efficiency of Ag(I) ions from the solid WPCB material was achieved using the following ILs: $[P_{4,4,4,4}][Cl]$, $[P_{4,4,4,14}][Cl]$, $[P_{8,8,8,8}][Br]$, $[N_{10,10,1,1}][C_2H_5COO]$, and $[N_{10,10,1,1}][H_2PO_4]$, with the addition of H_2O_2, TCCA, or (glycine + H_2O_2) in a single- or two-extraction stage. The best extraction of Cu(II), E_{Cu} = 68.9 wt%, was with $[P_{4,4,4,4}][Cl]$ + TCCA (8 g, two-extraction stage), and for E_{Cu} = 50.1 wt%, it was with $[N_{10,10,1,1}][C_2H_5COO]$ + TCCA (8 g, two-extraction stage). The best extraction of Zn(II) was E_{Zn} = 67.2–71.9 wt% with $[N_{10,10,1,1}][C_2H_5COO]$ in a single- or two-extraction stage. The best extraction of Al(III), E_{Al} = 81.2 wt%, was with $[P_{4,4,4,4}][Cl]$ + TCCA (8 g, two-extraction stage), and for E_{Al} = 52.5 wt%, it was with $[N_{10,10,1,1}][C_2H_5COO]$ + TCCA (8g, two-extraction stage). It has been demonstrated in a series of experiments that it is possible to use ILs or DESs for the extraction of metal ions from the solid WPCB e-waste after thermal pre-treatment to the liquid phase with a 60–100 wt% efficiency. However, the next step—the separation of copper, silver, or other metals from the final liquid solution—still has to be resolved.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/pr12030530/s1, 1. Synthesis of ILs; Figure S1: NMR of didecyldimethylammonium propionate, $[N_{10,10,1,1}][C_2H_5COO]$; Figure S2: NMR of didecylmethylammonium hydrogen sulphate, $[N_{10,10,1,H}][HSO_4]$; Figure S3: NMR of didecyldimethylammonium dihydrogen phosphate, $[N_{10,10,1,1}][H_2PO_4]$: Figure S4: NMR of tetrabutylphosphonium dihydrogen phosphate $[P_{4,4,4,4}][H_2PO_4]$.

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